REDUCTIVE AMINATION OF LACTOSE: UNUSUAL ^{13}C-N.M.R. SPECTROSCOPIC PROPERTIES OF *N*-ALKYL-(1-DEOXYLACTITOL-1-YL)AMINES*

PETER D. HOAGLAND, PHILIP E. PFEFFER, AND KATHLEEN M. VALENTINE
Eastern Regional Research Center†, Philadelphia, Pennsylvania 19118 (U.S.A.)
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ABSTRACT

Lactose was reductively aminated with selected alkylamines and sodium cyanoborohydride in boiling methanol in the presence of a weak organic acid. In alkaline solution, the *N*-alkyl-(1-deoxylactitol-1-yl)amines exhibited unusual behavior that was reflected by peak splitting in the ^{13}C-n.m.r. spectra of the β-D-galactopyranosyl- and D-glucitol-1-yl C-1 resonances. Anisotropic effects, documented by longitudinal relaxation-time measurements, suggest that motion in the carbohydrate region of the *N*-alkyl-(1-deoxylactitol-1-yl)amines is restricted by intermolecular interactions at high pH.

INTRODUCTION

Lactose is an underutilized sugar available from a renewable source, whey, which currently causes disposal problems for the cheese industry. Reductive amination of lactose offers access to *N*-substituted amino sugars that might have useful surface-active, metal-ion binding, or biological-growth properties[1]. Reductive amination with sodium cyanoborohydride has been successfully employed to fix lactose to a cellulose affinity-column[2]. For this investigation, sodium cyanoborohydride[3] was used selectively to reduce the imine initially formed by the condensation of an alkylamine with lactose and thereby minimize the formation of Amadori rearrangement-products. This route is an attractive alternative to both high- and low-pressure, catalytic hydrogenation[4-6].

RESULTS AND DISCUSSION

The reductive amination of lactose with an alkylamine and sodium cyanoborohydride in the environment of a weak organic acid proceeded smoothly in boiling methanol. T.l.c. monitoring of the reaction showed that the propionic or benzoic acid added did not promote the formation of Amadori rearrangement-products. The

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†Agricultural Research, Science and Education Administration, U.S. Department of Agriculture.

TABLE I

CHEMICAL SHIFTS FROM 15.04-MHz ^{13}C-N.M.R. SPECTRA, CARBOHYDRATE CARBON ATOMS[a]

Compound	*pH*	*β-D-Galactopyranosyl*						*1-Deoxy-D-glucitol-1-yl*					
		C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-1′*	*C-2′*	*C-3′*	*C-4′*	*C-5′*	*C-6′*
1	12.0	103.81	72.08	73.69	69.74	76.09	61.84	51.81	71.36	72.34	80.37	72.08	63.20
	1.7	103.35	71.88	73.31	69.55	75.96	62.04	50.38	68.58	71.30	79.33	71.88	62.88
2	1.5	103.42	71.95	73.37	69.62	76.03	62.10	50.58	68.64	71.49	79.20	71.95	63.01
	12.2	105.04	72.20	74.34	70.52	76.22	61.84	53.4	72.65	73.37	n.d.[b]	71.88	
		104.84	71.88	73.95	69.81	76.03	61.74		72.53	73.11		71.68	63.46
		104.58			69.55	75.89					72.92		
		104.06											
3	1.1	103.68	71.95	73.44	69.74	75.96	62.30	51.09	68.64	71.30	79.20	71.95	63.01
4	1.2	103.35	71.88	73.31	69.62	75.96	62.17	50.58	68.64	71.36	79.33	71.88	62.94
	12.2	104.91	71.75	73.63	70.33	76.93	61.58	53.49	72.53	73.11	n.d.[b]	72.53	64.11
		103.80	71.36		69.36	76.61		53.36	71.95			71.95	63.07
		103.61				75.77		51.87					
						75.18							
5	7	103.68	71.88	73.37	69.49	75.77	61.91	63.53	70.26	72.98	79.98	71.88	62.94
6	1.1	103.29	71.88	73.31	69.49	75.95	62.04	68.06	68.06	72.20	79.52	71.88	62.88
7	1.5	103.35	71.88	73.24	69.49	75.90	62.04	67.02	68.06	72.20	79.65	71.88	62.88
8	2.0	103.48	71.95	73.37	69.55	76.03	62.10	67.74	67.93	72.34	79.78	71.95	63.01
											80.04		

[a] δ (p.p.m.) referenced to internal 1,4-dioxane at 67.4 p.p.m. [b] n.d. = not detected.

TABLE II

CHEMICAL SHIFTS FROM 15.04-MHz ^{13}C-N.M.R. SPECTRA, ALKYL CARBON ATOMS[a]

Compound	*pH*	*C-N*	*C-N*	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*C-8*	*C-9*	*C-10*	*C-11*	*C-12*
1	12.0			51.55	22.73	12.04									
	1.7			50.38	19.94	11.20									
6	1.1	52.39	52.65	68.06	16.64	10.88									
	9.4	52.32	52.78	68.00	16.71	11.01									
2	1.5			48.96	26.55	26.29	28.75	31.73	22.80	14.70					
	12.2			50.0	29.53	27.65	29.98	32.12	22.99	14.57					
								32.31	23.44	14.76					
								32.70							
7	1.5	52.39	52.58	66.64	22.86	26.36	28.69	31.60	22.73	14.38					
	12.4	51.94	52.13	66.64	22.80	26.42	28.75	31.73	22.80	14.44					
4	1.2			48.95	26.74	26.36	[29.27	29.46	29.46	29.46	29.27]	25.32	34.84	179.18	
	12.2			49.80	29.66	27.52	[29.66	29.66	29.66	29.66	29.66]	26.81	38.53	184.30	
3	1.1			49.09	26.68	27.39	[29.98	30.31	30.50	30.50	30.50	30.31]	32.78	23.44	14.70
8	1.9	52.26	52.45	67.74	23.38	27.07	[29.92	30.18	30.44	30.44	30.44	30.18]	32.83	23.51	14.70

[a] δ (p.p.m.) referenced to internal 1,4-dioxane at 67.4 p.p.m.

TABLE III

T_1 VALUES FROM 15.04-MHz ^{13}C-N.M.R. SPECTRA, CARBOHYDRATE CARBON ATOMS OF COMPOUNDS **2**, **4**, LACTITOL, AND LACTOSE[a]

Compound	*pH*	*β-D-Galactopyranosyl*						*1-Deoxy-D-glucitol-1-yl*					
		C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C'-1*	*C'-2*	*C'-3*	*C'-4*	*C'-5*	*C'-6*
2	1.05	0.37	0.34	0.36	0.34	0.34	0.26	0.20	0.38	0.19	0.34	0.31	0.22
	7.95	0.11	0.14	0.14	0.12	0.13	0.12	0.08	0.09	0.14	0.13	0.14	0.09
	12.20	0.10	0.06	0.08	0.07	0.08	0.07	0.07	0.09	0.06	n.d.[c]	0.06	0.07
4	1.2	0.27	0.23	0.26	0.23	0.25	0.19	0.14	0.27	0.23	0.17	0.23	0.17
	11.5	0.17	0.17	0.17	0.14	0.16	0.15	0.10	0.15	0.14	n.d.[c]	0.15	0.11
Lactitol	12.0	0.54	0.53	0.52	0.43	0.51	0.47	0.46	0.49	0.51	0.54	0.54	0.42
α-Lactose[b]	1.75	0.42	0.44	0.46	0.34	0.43	0.30	0.44	0.43	0.43	0.46	0.43	0.24
β-Lactose[b]	1.75	0.42	0.44	0.46	0.34	0.43	0.30	0.46	0.47	0.48	0.46	0.43	0.24

[a]Values in sec. [b]Saturated solution, 20% D_2O. [c]n.d. = not detected.

TABLE IV

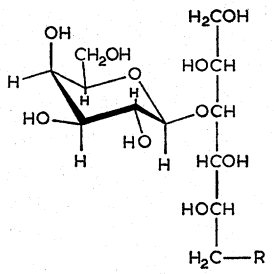
T_1 VALUES FROM 15.04-MHz ^{13}C-N.M.R. SPECTRA, ALKYL CARBON ATOMS FOR COMPOUNDS **2** AND **4**[a]

Compound	*pH*	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*C-8*	*C-9*	*C-10*	*C-11*
2	1.05	0.36	0.53	0.51	0.96	1.43	2.16	3.55				
	7.95	0.14	0.29	0.23	0.48	0.77	1.09	1.97				
	12.20	0.10	0.11	0.13	0.24	0.47	1.09	1.26				
4	1.2	0.23	0.30	0.31	0.34	0.34	0.34	0.34	0.34	0.59	0.56	n.d.[b]
	11.5	0.17	0.23	0.28	0.38	0.38	0.38	0.38	0.38	0.68	0.81	n.d.[b]

[a]Values in seconds. [b]n.d. = not detected.

amine salts could be purified by precipitation from methanol with acetone or ether. Attempts to remove co-precipitated inorganic material by passage of a water solution of the amine salt through a column of Bio-Gel P2 were partially successful. Final products typically contained 5% of ash, precluding characterization by conventional elemental analysis. In addition, small amounts of higher molecular-weight substances, probably alkyl-*N*,*N*-bis(1-deoxylactitol-1-yl)amines, were recovered from the void volumes.

Characterization of the alkyl-*N*-(1-deoxylactitol-1-yl)amine salts was accomplished by ^{13}C-n.m.r. spectroscopy under both acid and alkaline conditions, and by field-desorption mass spectrometry. The changes in ^{13}C-chemical shifts produced by protonation of the nitrogen atom under acid conditions (Tables I and II), the changes in T_1 values as a function of pH (Tables III and IV), and the chemical-shift values for lactitol, 1-deoxy-1-methylamino-D-glucitol, dipropylamine, and dibutylamine made possible the unequivocal assignment of chemical-shift values to every carbon



1 R = $NHCH_2CH_2CH_3$
2 R = $NH(CH_2)_6CH_3$
3 R = $NH(CH_2)_{11}CH_3$
4 R = $NH(CH_2)_{10}CO_2H$
5 R = OH
6 R = $^{+}NMe_2CH_2CH_2CH_3$
7 R = $^{+}NMe_2(CH_2)_6CH_3$
8 R = $^{+}NMe_2(CH_2)_{11}CH_3$

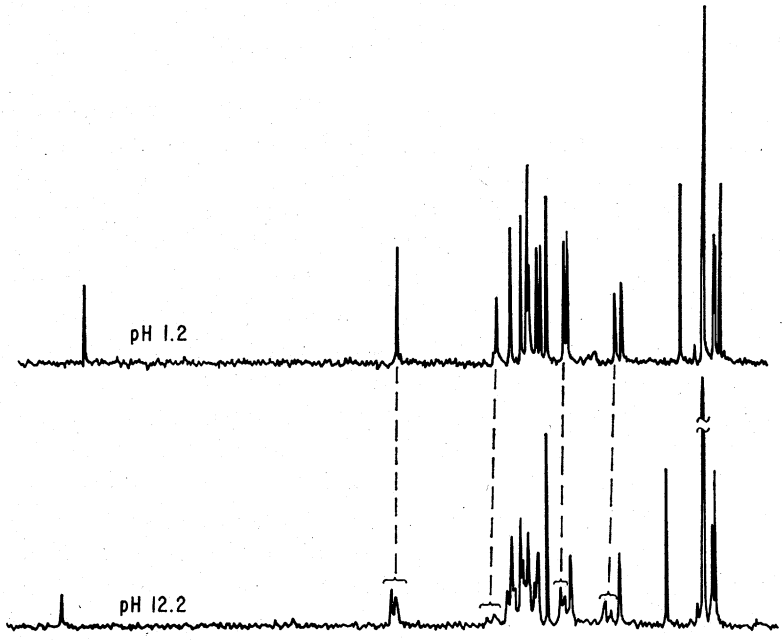


Fig. 1. 15.04-MHz ^{13}C-n.m.r. spectra of *N*-(1,deoxylactitol-1-yl)-11-aminoundecanoic acid at high and low pH, 20% solution at 32°.

atom of each amine salt, with the exception of some interior carbon atoms of the alkyl groups of compounds **3** and **4**.

The chemical shifts assigned to the carbon atoms of the β-D-galactopyranosyl group agree well with published values[7,8]. Furthermore, firm assignments for C-3 and C-5 for α- and β-glucopyranosyl residues of α- and β-lactose have been made by a differential, deuterium isotope-shift method recently developed in this laboratory[9].

Quite unexpected was the peak splitting in the ^{13}C-n.m.r. spectra for compounds **2**, **3**, and **4** in solution made alkaline with sodium hydroxide. This condition is illustrated in Fig. 1 with 11-[(1-deoxylactitol-1-yl)amino]undecanoic acid (**4**). With *N*-(1-deoxylactitol-1-yl)dodecylamine (**3**) under alkaline conditions, striking degradation of the 70–90 p.p.m. region of the spectrum made impossible the assignment of shift values to the carbohydrate carbon atoms. As may be seen in Tables I and II, for every compound at high pH, except lactitol (**5**) and *N*-(1-deoxylactitol-1-yl)propylamine (**1**), the C-4′ resonance peak disappears. Moreover, at low pH, this peak is split for the *N*-(1-deoxylactitol-1-yl)-*N*,*N*-dimethyldodecylammonium ion (**8**). In many instances at high pH, C-1, C-1′, and C-6′ are very prone to splitting, followed by C-4, C-5, and eventually the remaining carbohydrate carbon atoms. Peak splitting is favored by increased length of alkyl chain and by methylation of the nitrogen atom. Peak splitting is favored at high pH (sodium hydroxide) and was found to be reversible for compound **4** on going from basic to acid to basic conditions. Of further interest is that the *N*-methyl groups of compounds **6**–**8** yield two chemical shifts at all pH values (Table II). Only single shifts for methyl groups of *N*-alkylsulfobetaines have been observed in this laboratory, and for methyl groups of lecithins by Lee *et al.*[10].

The ^{13}C-n.m.r. spin-relaxation time (T_1) is an established and useful parameter for studying internal molecular mobility in lactose[11]. To gain insight into possible structures that might exhibit ^{13}C resonance peak-splitting, relaxation times were determined for *N*-(1-deoxylactitol-1-yl)heptylamine (**2**). As shown in Table IV, the T_1 values of alkyl carbon atoms increase from the amine end towards the terminal methyl group. Such a mobility gradient has been reported for molecules having a constituent alkyl group[10,12]. This gradient is believed to arise from segmental motion that increases toward the free end of the chain[12]. In addition, the T_1 value for each carbon atom of the heptyl chain decreases as the pH increases. A similar relationship also holds for the T_1 values for the carbohydrate carbon atoms (Table III). There is a large decrease in the T_1 value for each carbon atom on going from acid to alkaline conditions. The T_1 values at pH 1.05 for the carbohydrate carbon atoms of **2** are only slightly smaller than those for lactitol and for lactose (Table III). This difference may be attributed to the slightly lower tumbling-rate expected for the larger (1-deoxylactitol-1-yl)amine molecule. The T_1 values of C-4 of the β-D-galactopyranosyl ring are distinctly low for lactitol and for lactose. In the case of lactose, Czarniecki and Thornton[11] have interpreted a low C-4 T_1 value as originating from a favored rotation about the C-1–C-4 axis of the β-D-galactopyranosyl ring. Because the (1-deoxylactitol-1-yl)amines **2** and **4** do not have uniquely low T_1 values at C-4 of the β-D-galactopyranosyl group, favored rotation about the C-1–C-4 axis does not obtain. The lactitol-1-ylamines **2** and **4** have molecular motions different from those of lactose and of (the more closely related) lactitol. No conspicuous features appear in the T_1 values for the carbohydrate carbon atoms of the (1-deoxylactitol-1-yl)amines **2** and **4**, other than the general decrease with increasing pH. The longitudinal relaxation-times of the methine carbon atoms of the galactopyranosyl portion of *N*-(1-

deoxylactitol-1-yl)heptylamine (**2**) at high pH and 32° (Table III) range from 0.06 to 0.10. For similar carbon resonances in micelles of chloroplast lipids in D_2O at 38°, Johns *et al.*[12] reported a T_1 value of 0.06. In a noninteracting molecule, *N*-acetylneuraminyl-lactose at 28°, the methine carbon resonances of the interior galactopyranosyl group have T_1 values that range[11] from 0.16 to 0.19. Clearly, motion of the carbohydrate carbon atoms of the alkyl-*N*-(1-deoxylactitol-1-yl)amines at high pH has been decreased.

The ^{13}C-n.m.r. literature contains examples of micellar and bilayer systems that exhibit line-broadening attendant with decreased dipole–dipole relaxation-times[10,12]. However, peak splitting is not characteristic of the intermolecular interactions that determine formation of micelles or bilayers[10,12–15]. Therefore, our observations of peak splitting and decreased molecular motion at high pH values point to unusual solution properties of alkyl-*N*-(1-deoxylactitol-1-yl)amines and their methylated derivatives. The nature of the peak splitting suggests that the glycosidic bond, and especially C-4′ of the glucitol-1-yl group, is involved in the molecular interactions. The pH effect suggests the involvement of hydroxide ions and/or sodium ions and not the charge on the nitrogen atom, as the quaternary (1-deoxylactitol-1-yl)-amines do not lose their charge at high pH. A minimum hydrophobic contribution to the molecular interactions is strongly indicated from the effects upon peak splitting of alkyl chain-length and *N*-methylation. The new, lower-mobility states arising from these molecular interactions are required to have unusually low rates of interconversion in order for peak splitting to occur. Moreover, distinct peak-splitting is manifested largely in the resonance of C-1 of the galactopyranosyl and 1-deoxyglucitol-1-yl groups, and indicates that the central domain of the molecule exists in two slowly equilibrated states. Further investigations are required to explain completely the unique peak-splitting of the carbon resonances observed for alkyl-*N*-(1-deoxylactitol-1-yl)amines and their quaternized derivatives in alkaline solution.

EXPERIMENTAL

Materials and methods. — β-Lactose, propylamine, heptylamine, 1-butanol, methyl iodide, and propanoic acid were products of Eastman*. Dodecylamine was obtained from Armour Industrial Chemicals. Benzoic acid, potassium hydrogencarbonate, and abs. methanol were reagent-grade products (J. T. Baker). Sodium cyanoborohydride and 11-aminoundecanoic acid were obtained from Aldrich.

^{13}C-N.m.r. spectra were acquired with a JEOL FX60Q 15.04-MHz n.m.r. instrument equipped with a 16K data point, dedicated computer used for Fourier transformation of the free-induction decay accumulated typically after several thousand pulses. The solvent was 79% H_2O and 20% D_2O, with 1% of 1,4-dioxane as the internal standard. Concentrations were 20%, and the pH was adjusted with

*Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

concentrated sodium hydroxide or hydrochloric acid. Each spectrum was obtained with a 58° pulse, a repetition rate of 3 sec, a 4000-Hz sweep-width, and complete proton-noise decoupling. The T_1 values were obtained from inversion-recovery experiments employing a 180° — t — 90° — T pulse sequence with T = 10 sec and t = 0.01, 0.05, 0.10, and 0.30 sec.

T.l.c. was performed with small plates (6 cm migration) of silica gel G with 6:3:1 1-butanol–acetic acid–water. A ninhydrin spray (2% in acetone) was used for detection of amino groups. This spray produced a red color for the secondary amines, and a blue color for the primary amines examined as controls. Carbohydrate material was detected with 1-naphthol and 50% sulfuric acid sprays.

Theoretical mass-values for MH^+ and for MNa^+ were obtained with a Varian MAT 311A field-desorption mass spectrometer*.

N-(*1-Deoxylactitol-1-yl*)*propylamine, propionate salt.* — A mixture of β-lactose (3.42 g, 10 mmol, Eastman), propanoic acid (1.45 g, 20 mmol), propylamine (0.82 mL, 10 mmol), and methanol (40 mL) was boiled under reflux and treated dropwise with methanolic sodium cyanoborohydride (0.8 g, 12 mmol;15 mL). After boiling for 14 h, the solvent was removed and the residue washed with acetone and collected; yield 4.92 g. The material was dissolved in hot methanol (10 mL) and the solution was added to 200 mL of acetone with rapid stirring. The white precipitate was collected, washed with ether, and dried in a stream of nitrogen; yield 3.03 g (66%), $[\alpha]_D^{25}$ +4.97° (*c* 2.44, water); t.l.c. showed one spot, both carbohydrate- and ninhydrin-positive. Theoretical-mass peaks of $[C_{15}H_{31}NO_{10} + H^+]$ = 386 and $[C_{15}H_{31}NO_{10} + Na^+]$ = 408 were obtained.

N-(*1-Deoxylactitol-1-yl*)*heptylamine, benzoate salt.* — A mixture of β-lactose (3.42 g, 10 mmol), heptylamine (1.5 mL, 10 mmol), benzoic acid (2.44 g, 20 mmol), and methanol (40 mL) was boiled under reflux and treated dropwise with sodium cyanoborohydride (0.8 g, 12 mmol in 15 mL of methanol). After 24 h, the solvent was removed by flash evaporation from the clear amber solution. The residue was washed with acetone and ether, and dried with nitrogen; yield 5.06 g (90%). Further purification by reprecipitation from methanol and acetone and by passage through a column of Biogel P-2 gave material that gave one spot, both carbohydrate- and ninhydrin-positive, by t.l.c.; $[\alpha]_D^{25}$ +15.8° (*c* 1.93, water). Theoretical-mass peaks of $[C_{19}H_{39}NO_{10} + H^+]$ = 442 and $[C_{19}H_{39}NO_{10} + Na^+]$ = 464 were obtained.

N-(*1-Deoxylactitol-1-yl*)*dodecylamine, benzoate salt.* — A mixture of β-lactose (3.42 g, 10 mmol), dodecylamine (1.85 g, 10 mmol), benzoic acid (2.44 g, 20 mmol), and methanol (40 mL) was boiled under reflux and treated dropwise with sodium cyanoborohydride (0.08 g, 12 mmol in 15 mL of methanol). Solvent was removed by flash evaporation after 22 h from the clear, dark-amber solution. The residue was broken up with acetone and washed with ether. Drying under nitrogen gave 6.90 g of material (109% yield); ν_{max}, 1600 cm^{-1} (carboxylate). T.l.c. showed one major

*Cationization of carbohydrates by trace amounts of alkaline cations can greatly increase the sensitivity of field-desorption mass spectrometry in a manner not well understood at present[17].

component, ninhydrin- and carbohydrate-positive, and no lactose or dodecylamine; $[\alpha]_D^{25}$ +1.21° (*c* 8.20, water). Theoretical-mass peaks of $[C_{24}H_{49}NO_{10} + H^+] = 512$ and $[C_{24}H_{49}NO_{10} + Na^+] = 534$ were obtained.

11-[(1-Deoxylactitol-1-yl)amino]undecanoic acid. — A mixture of β-lactose (3.42 g, 10 mmol), 11-aminoundecanoic acid (2.01 g, 10 mmol), propanoic acid (0.75 mL, 10 mmol), and methanol (40 mL) was boiled under reflux and treated dropwise with sodium cyanoborohydride (0.8 g, 12 mmol in 15 mL of methanol). After 22 h, a gummy mass had settled out. The solvent was decanted off, the mass was dissolved in water (10 mL), and the solution was dropped into acetone (400 mL). A white, gritty precipitate formed, which was collected, washed with ether, and dried under nitrogen; yield 3.05 g (58%); $[\alpha]_D^{25}$ +2.21° (*c* 1.74, water); t.l.c. showed one spot, both carbohydrate- and ninhydrin-positive. Theoretical-mass peaks of $[C_{23}H_{45}NO_{12} + H^+] = 528$ and $[C_{23}H_{45}NO_{12} + Na^+] = 550$ were obtained.

Quaternization. — The procedure of Chen and Benoiton was used[16]. The alkyl *N*-(1-deoxylactitol-1-yl)amine salt (1 mmol), potassium hydrogencarbonate (1 g), methyl iodide (1 mL), and methanol (20 mL) were mixed together at room temperature. The solvent and excess of methyl iodide were removed by flash evaporation and the residue was taken up in methanol. The product was precipitated by addition of acetone, washed with ether and dried, and then subjected to ^{13}C-n.m.r. spectroscopic analysis.

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